

Degradation of Starch Polymers by Microwave Energy¹

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ABSTRACT

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Aqueous starch suspensions (10, 20, and 30%) at neutral pH were heated 16, 18, and 20 min at 0.18-mA microwave energy in sealed glass tubes. The most obvious change was that the color of the hydrolysates became darker as temperature and pressure increased. Aromas of heated suspensions ranged from starchy to burnt and caramel-like. Total acidity increased and

pH decreased concurrently. Qualitative analysis by paper chromatography revealed that the starch hydrolysates contained oligosaccharides ranging from G₁ to G₈ and higher. Total soluble sugar, total reducing sugars, and glucose concentrations as high as 93.3, 53.4, and 23.9% were noted in the hydrolysates.

Kirchoff discovered in 1811 that heating potato starch with dilute sulfuric acid transformed the starch into sugarlike substances, and De Saussure showed that the potato sugar was identical to grape sugar or glucose (Kerr 1950). Within a year, starch-sugar manufacturing plants using Kirchoff's discovery were operating in France and Germany. In the United States, no commercial starch-sugar plants operated on that principle until about 1873 (Kerr 1950). Amylase enzymes have been available during the last two decades for more efficient production of sugars from starch with fewer undesirable by-products. In practice, starch is partially hydrolyzed with acid and the hydrolysis is completed by amylase enzymes (Whelan 1957).

Starch hydrolysis has been studied in a closed system using water at a neutral pH (Calentine 1967, Lorenz and Johnson 1972). Calentine (1967) heated 1% starch suspensions at different temperatures in stainless steel tubes. Lorenz and Johnson (1972) hydrolyzed 3% starch suspensions in glass tubes and identified the compounds in the hydrolysates. In both studies, the starch suspensions were heated for 1 hr by a convectional heating system.

This investigation used microwave energy to reduce the heating period while hydrolyzing starch suspensions at neutral pH.

MATERIALS AND METHODS

Starch was prepared from hard red winter wheat flour by Wolf's method (1964) and defatted by Schoch's method (1942). It was analyzed for moisture, protein, and total fat by standard AOAC methods (1970).

Starch suspensions (10, 20, and 30%) were made in distilled water, and 30 ml of suspension was injected into each heavy-walled glass tube with a syringe. Starch suspensions in the glass tubes were frozen with acetone and dry ice, then evacuated and sealed with an oxygen flame. The starch suspensions were allowed to thaw and attain room temperature before being placed horizontally on a glass stand on a rotating plastic disc in the microwave oven (Despatch Oven Company, heating capacity 1.2 k). The tubes were heated at 0.18 mA for 16, 18, and 20 min. Temperature inside the tubes during heating was estimated with temperature indicators (Tempil Division, Big Three Industrial Gas and Equipment Company). After heating, the tubes were cooled, and the hydrolysate was centrifuged at 10,000 rpm for 10 min. The volume of the hydrolysate was measured and the sugar concentration determined.

A 5-ml aliquot of the hydrolysate was neutralized with 0.01N NaOH and placed on a DEAE-cellulose column. Sugars were eluted with distilled water at a flow rate of 1 ml/min, maintained with an automatic solution metering pump (Model 746, Beckman Company); 1,000 ml was collected, and the eluate was concentrated to 50 ml at 40°C under reduced pressure.

Qualitative analysis of the sugar concentrates was done by paper chromatography using Whatman No. 1 paper and a *n*-propanal-ethyl acetate-water (6:1:3 v/v) solvent system (Travelyan et al 1950) for 40 hr. Samples of 10, 20, and 30% starch suspensions were applied to the paper chromatogram in 200, 100, and 50 μ l amounts respectively.

Sugar concentrates were analyzed for total sugars, reducing sugars, and glucose. Total sugar was determined by the phenol-sulfuric acid method (Dubois 1951). The Somogyi micro copper method (Hodge and Hofreiter 1962) was used to determine reducing sugars, and glucose was determined enzymatically by the glucose-oxidase method (Shetty et al 1974). The amounts were calculated as percentage of initial starch.

RESULTS AND DISCUSSION

Starch in water heated with microwave energy was hydrolyzed by high temperatures and pressures inside the glass tubes. The appearance of the solutions, especially the liquefying and coloring, was the most obvious change during hydrolysis of starch suspensions. Starch solutions after heating went from viscous to watery and their color varied from milky white to dark brown as the duration of heating increased from 16 to 20 min. The hydrolysates had characteristic aromas ranging from starchy to burnt and caramel-like. Calentine (1967) and Lorenz and Johnson (1972) reported similar changes.

Temperature and Pressure

The temperature of starch slurries increased with duration of heating at all concentrations (Table I). Temperature ranged from below 170°C in 10% starch suspensions heated for 16 min to 191–198°C in 30% starch suspensions heated 20 min. As the concentration of starch increased from 10 to 30%, the temperature of slurries increased at any given time of heating, which was probably related to amounts of water in the starch suspensions. In other words, the less water present, the shorter the time needed to raise the temperature of the suspension.

Vapor pressure inside the tubes was calculated from steam tables corresponding to the temperature (Table I).

TABLE I
Temperature and Pressure Inside Glass
Tubes During Starch Hydrolysis

Concentration of Starch Suspension (%)	Duration of Heat Treatment (min)	Temperature Range (°C)	Vapor Pressure (lbs/in ²)
10	16	Below 170 ^a	Below 115 ^a
10	18	170–173	115–123
10	20	173–177	123–136
20	16	173–177	123–136
20	18	177–184	136–159
20	20	184–191	159–186
30	16	177–184	136–159
30	18	184–191	159–186
30	20	191–198	186–216

^aMean of two replications.

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pH and Total Acidity of Starch Hydrolysates

The pH of starch suspensions decreased with increasing duration of heat treatment and starch concentration (Table II), probably because acids formed during heating. Lorenz and Johnson (1972) reported the formation of formic, acetic, propionic, isobutyric, isovaleric, valeric, isocaproic, and caproic acid during heating. Air oxidation of the corresponding aldehydes is a possible source of the acids because vacuum in the tubes was not complete. They also pointed out that the concentration of C₅ and C₆ acids (isovaleric, valeric, isocaproic, and caproic) that predominated at low temperatures decreased as the temperature increased; C₁ and C₂ acids (formic and acetic acid) increased as the temperature increased.

The total acidity of 10, 20, and 30% starch hydrolysates heated for 16 min was 0.003, 0.014, and 0.28 meq (Table II), respectively. As the duration of heating increased from 16 to 20 min, total acidity increased at all concentrations (Table II).

TABLE II
pH and Acidity of Starch Suspensions
After Heat Treatment

Concentration of Starch Suspension (%)	Duration of Heat Treatment (min)	pH	Total Acidity (meq/5 ml)
10	16	4.5 ^a	0.003 ^a
10	18	5.2	0.006
10	20	3.9	0.010
20	16	3.8	0.014
20	18	3.6	0.027
20	20	3.4	0.042
30	16	3.8	0.028
30	18	3.2	0.071
30	20	3.1	0.084

^aMean of two replications.

TABLE III
Effect of Duration of Heating and Concentration of Starch
on the Formation of Total Sugar, Reducing Sugar, and Glucose

Concentration of Starch Suspension (%)	Duration Heat Treatment (min)	Total Soluble Sugar/Starch (%)	Reducing Sugar/Starch (%)	Glucose/Starch (%)
10	16	47.3	3.1	0.6
10	18	60.2	5.5	1.5
10	20	79.8	10.3	3.4
20	16	62.1	7.9	0.8
20	18	79.8	18.0	3.4
20	20	88.7	33.4	11.1
30	16	74.3	19.3	1.8
30	18	93.3	41.7	15.1
30	20	90.4	53.4	23.9

TABLE IV
Analysis of Variance of Effect of Duration of Heating and Concentration
of Starch on Formation of Total Sugar, Reducing Sugar and Glucose

Source of Variation	Degrees of Freedom	Mean Square		
		Total Sugar	Reducing Sugar	Glucose
Starch concentration	2	847.8 ^a	1529.40 ^a	221.3 ^a
Time of heating	2	976.9 ^a	743.40 ^a	205.0 ^a
Concentration × time	4	68.4 ^a	107.20 ^a	51.0 ^a
Error		3.5	0.70	0.5

^aSignificant at 0.05.

Qualitative Analysis by Paper Chromatography

Analysis of starch hydrolysates by paper chromatography showed that the heat treatments caused hydrolysis of starch and formation of various oligosaccharides. The effect of microwave heat treatment of 10% starch suspensions for 16 min was almost undetectable by paper chromatography. Heat treatment of 10% starch suspensions for 18 and 20 min, however, produced a homologous series of oligosaccharides ranging from G₁ to G₈ and higher. Sugars from G₁ to G₈ and higher were detected on the chromatograms in 20 and 30% starch hydrolysates heated for 16, 18, or 20 min.

Total Sugars

Heating of 10, 20, and 30% starch suspensions for 16 min produced 47.37, 62.17, and 74.3% total sugars (Table III), respectively. As the duration of heating increased from 16 to 20 min, the concentration of total sugar increased in 10 and 20% starch suspensions. However, in 30% suspensions, production of total sugar was up to 93.3% after 18 min but dropped to 90.4% after 20-min heating, probably because sugars were destroyed. Analysis of variance (Table IV) indicated that the concentration of starch and the duration of heating significantly affected ($P = 0.05$) on production of total sugars.

Reducing Sugars

Reducing sugars increased with duration of heating at all concentrations (Table III). However, reducing sugars were formed much faster in the 30% than in the 10% starch suspensions. Concentration of starch and duration of heating significantly ($P = 0.05$) affected the production of reducing sugars (Table IV).

Glucose

Starch suspensions heated 16 min had little glucose; however, as the duration of heating increased to 20 min, the glucose concentration increased from 0.6 to 3.4% in 10% suspensions, from 0.8 to 11.1% in 20% suspensions, and from 1.8 to 23.9% in 30% starch suspensions (Table III). Concentration of starch and duration of heating significantly affected ($P = 0.05$) formation of glucose (Table IV).

Sugar syrups of high dextrose equivalent can be produced with less time and energy by microwave energy than by conventional methods.

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